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桥联钌苯和锇苯的合成及其化学与物理性质研究

Studies towards the Synthesis, Chemical and Physical Properties of Bridged Ruthenabenzenes and Osmabenzenes

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Studies towards the Synthesis, Chemical and Physical Properties of Bridged Ruthenabenzenes and Osmabenzenes

A Dissertation Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of Doctor Philosophy

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摘　要

共轭桥联金属有机配合物因其特殊的光电性能，在金属有机化学研究领域中居重要地位。设计合成具有特殊性能的桥联金属配合物成为研究的热点之一。金属苯作为一类特殊的芳香体系，其潜在的光电性能逐渐引起了学术界的关注。将金属苯引入到桥联共轭体系中，设计合成结构新颖的桥联金属苯，将为今后的光电材料应用研究奠定基础。

本文主要设计合成了三类桥联钌苯和锇苯，并对其电化学性质和紫外光谱进行了初步研究。主要研究内容和结果如下：

第一章为绪论，较系统地介绍了共轭桥联金属配合物的合成和光电性能研究进展，简明阐述了金属苯的研究现状，结合本课题组的研究方向提出了相关的科学问题。

第二章研究了氮杂芴型桥联双金属苯的合成与表征，并初步探讨了其电化学和紫外光谱性质。首先，按照文献方法合成了五个桥联氮杂芴型配体，分别为：$C_{11}H_8N_3$-R-$C_{11}H_8N_3$ (R = none, BL_1; 1,4-C_6H_4, BL_2; 4,4'-C_6H_4-C_6H_4, BL_3; 4,4'-$C_6H_4CH_2C_6H_4$, BL_4)和4,4'-$C_{13}H_7N_4$-C_6H_4-$C_{13}H_7N_4$ (BL_5)。其次，利用这些桥联配体分别与钌苯 $[Ru(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]Cl$ 和锇苯 $[Os(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]OH$ 反应合成了十个桥联双金属苯 $[BL_n\{M(CHC(PPh_3)CHC(PPh_3)CH)Cl(PPh_3)\}_2][PF_6]_4$ (M = Ru, Os)，并对其结构进行了系统表征，其中由BL_4桥联的双钌苯和双锇苯的结构为X-射线衍射单晶实验所证实。此外，还对部分桥联双金属苯的紫外光谱进行了初步研究，结果表明这些配合物的紫外吸收光谱特征与$[M(bpy)_3]^{2+}$(M = Ru, Os)及相关配合物的光谱特征较相似，在420 nm~450 nm区域出现明显的$d\pi(M)\rightarrow\pi^*$(MLCT)电子跃迁。

第三章研究了双异腈和三异腈桥联金属苯的合成、表征及其电化学、紫外光谱性质，并初步探讨了形成4-位为氯取代锇苯的反应机理。首先研究了锇杂环配合物$[Os(CH=C(PPh_3)CH(OH)-\eta^2-C\equiv CH)Cl_2(PPh_3)_2]$与2,6-二甲基苯基异腈、对甲苯磺酰基甲基异腈、1氢-苯并三氮唑甲基异腈、1,1,3,3-四甲基丁基异腈的反应，得到四个单异腈配位的4-位为氯取代的稳定锇苯。进而按文献方法合成了四个双齿

异腈，分别为：1,4-对苯二异腈，4,4'-联苯二异腈，4,4'-二异腈苯基醚，4,4'-二异腈苯基甲烷。另外，参考并改进文献方法以4-硝基苯乙酮为原料通过Aldol加成、分子内自缩合和Pd/C还原反应合成了1,3,5-三(4'-氨基苯基)苯，最后在Ugi条件下合成了三齿异腈1,3,5-三(4'-异腈苯基)苯。并利用上述双齿和三齿异腈分别与金属苯[M(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)$_2$]X (M = Ru, X = Cl; M = Os, X = OH)和锇杂环配合物[Os(CH=C(PPh$_3$)CH(OH)-η^2-C≡CH)Cl$_2$(PPh$_3$)$_2$]分别通过配体取代和亲核加成反应成功地合成了桥联双金属苯(μ-CN-R-NC)[M(CHC(PPh$_3$)CHC(Y)CH)Cl(X)(PPh$_3$)]$_2$[2Z] (M = Ru, Os, X = Cl, Y = PPh$_3$, Z = PF$_6$; M = Os, X = PPh$_3$, Y = Cl, Z = Cl; R = 1,4-C$_6$H$_4$, 4,4'-C$_6$H$_4$C$_6$H$_4$, 4,4'-C$_6$H$_4$CH$_2$C$_6$H$_4$, 4,4'-C$_6$H$_4$OC$_6$H$_4$)和三金属苯(μ-(CN)$_3$-R)[M(CHC(PPh$_3$)CHC(Y)CH)Cl(X)(PPh$_3$)]$_3$[3Z] (M = Ru, Os, X = Cl, Y = PPh$_3$, Z = PF$_6$; M = Os, X = PPh$_3$, Y = Cl, Z = Cl: R = 1,3,5-(4'-C$_6$H$_4$)$_3$)。为了作电化学实验对照，用类似方法合成了两个桥联锇杂双呋喃[μ-(CN-R-NC){Os(CHC(PPh$_3$)C(OEt)O)Cl(PPh$_3$)$_2$}$_2$Cl$_2$] (R = 1,4-C$_6$H$_4$, 4,4'-C$_6$H$_4$OC$_6$H$_4$)。对以上这些化合物进行了系统表征，其中部分配合物的结构还经过X-ray单晶实验所证实。运用循环伏安法对部分配合物的电化学性质进行了研究，结果表明1,4-对苯二异腈桥联的4-位为氯取代的锇苯中两个锇中心有较强的相互作用，其它的双金属苯都含有多个氧化还原单元。此外，还初步研究了其紫外光谱，结果表明这些配合物在310 nm~360 nm区域出现MLCT跃迁。

第四章研究了双金属亚丙二烯型配合物的合成、表征及其电化学和紫外光谱性质。首先在NaPF$_6$存在下，*cis*-OsCl$_2$(dppm)$_2$和*cis*-RuCl$_2$(dppe)$_2$分别与9-羟基-9-乙炔基-4,5-双氮杂芴反应合成了[OsCl(dppm)$_2$=C=C=(4,5-diazafluore-9-yl)][PF$_6$]和[RuCl(dppe)$_2$=C=C=(4,5-diazafluore-9-yl)][PF$_6$]，然后分别与金属苯通过配体取代反应合成了四个双金属亚丙二烯型配合物[M$_1$Cl(PΛP)$_2$=C=C=(4,5-diazafluoren-9-yl){M$_2$(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl(PPh$_3$)}][PF$_6$]$_3$ (M$_1$ = Os, Ru; M$_2$ = Os, Ru; PΛP = dppm, dppe)。此外，*cis*-RuCl$_2$(dppe)$_2$与苯乙炔反应得到亚乙烯基配合物*trans*-[(dppe)$_2$(Cl)Ru=C=CHPh][PF$_6$]，然后在碱性条件下，该乙烯基配合物与9-乙炔基-9-芴醇和9-羟基-9-乙炔基-4,5-双氮杂芴反应合成了两个末端由9-芴基和4,5-双氮杂-9-芴基修饰的单钌炔-亚丙二烯型配合物*trans*-[(dppe)$_2$Ru(C≡CPh)Ru=C=C=(R)][PF$_6$] (R = fluoren-9-yl, 4,5-diazafluoren-9-

yl)。按照类似方法，采用1,4-对苯二乙炔和1,3-间苯二乙炔先后分别与*cis*-$RuCl_2(dppe)_2$和炔醇(9-乙炔基-9-芴醇、9-羟基-9-乙炔基-4,5-双氮杂芴)反应合成了桥联双钌亚丙二烯型配合物 *trans*-{$(dppe)_2[=C=C=(R^1)]Ru$-(C≡C-R^2-C≡C)Ru[$(=C=C=(R^1)(dppe)_2]$}$[PF_6]_2$ (R^1 = fluoren-9-yl, 4,5-diazafluoren-9-yl, R^2 = 1,4-phenylene, 1,3-phenylene)，并对其结构进行了系统表征。运用循环伏安法对部分配合物的电化学性质进行了研究，结果表明1,4-对苯二乙炔基桥联的双钌亚丙二烯配合物中两个钌中心有较强的相互作用。此外，还初步研究了这些金属杂亚丙二烯的紫外光谱性质，发现这些配合物在较宽的波长范围内(200 nm~900 nm)有较强的吸收峰，有望用于太阳能电池敏化染料研究。

第五章对论文的工作进行了总结，并在此基础上对今后研究工作进行了展望。

关键词：桥联双金属苯；双氮杂芴；多齿异腈桥；双金属亚丙二烯型配合物；电子传递；光电性质

Abstract

Organometallic complexes with π-conjugated bridges play an important role in organometallic chemistry research for their special photoelectronic properties in fields including liquid crystals, luminescence, optical nonlinearity and electronic communications. The rational design and synthesis of novel complexes linked with π-conjugated bridges, which have special properties, have become one of the hottest subjects in the fields of molecular electronics in recent years. As special aromatic compounds, the metallabenzenes have gained more and more importance due to their latent photoelectronic properties. Metallabenzenes bridged with π-conjugated ligands constitute a particularly attractive class of candidates for nanoscopic molecular devices. Therefore, particular efforts have been directed toward the preparation and characterization of bridged metallabenzenes, so as to lay a foundation for the further research of photoelectric materials.

In the work described herein, the synthesis of three kinds of bridged metallabenzenes have been described. Additionally, the electrochemical and ultraviolet spectral properties of these complexes have also been investigated.

In chapter **1**, the research progress on the synthesis and photoelectrical properties of organometallic complexes with π-conjugated bridges is reviewed systematically, and the present research situation of bismetallabenzenes is also introduced briefly. Based on the above related research background, the research significance and related results of this dissertation are presented.

In chapter **2**, the synthesis, characterization of diazafluorene bridged bismetallabenzenes and related complexes are described. Additionally, the electrochemical and ultraviolet spectral properties of some of these complexes are studied preliminarily. According to the reported method, a total of five polypyridyl ligands based on diazafluorene ($C_{11}H_8N_3$-R-$C_{11}H_8N_3$ (R = none, BL_1; 1,4-C_6H_4, BL_2; 4,4'-C_6H_4-C_6H_4, BL_3; 4,4'-$C_6H_4CH_2C_6H_4$, BL_4) and 4,4'-$C_{13}H_7N_4$-C_6H_4-$C_{13}H_7N_4$ (BL_5)) have been preparared. A total of ten bismetallabenzenes $[BL_n\{M(CHC(PPh_3)CHC(PPh_3)CH)Cl(PPh_3)\}_2][PF_6]_4$ (M = Ru, Os) linked by bridging ligands based on diazafluorene have been synthesized by reactions of two equivalents of metallabenzenes $[M(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)_2]X$ (M = Ru, X = Cl, M = Os; X = OH) with above polypyridyl ligands in the presence of NH_4PF_6,

which have been fully characterized by ^{1}H, ^{13}C, ^{31}P NMR spectrometry. Moreover, the structures of two complexes have been determined by X-ray diffraction. The ultraviolet absorption spectra of these complexes exhibit a prominent band in the region 420~450 nm that is characteristic of $d\pi\rightarrow\pi^{*}$(MLCT) band. These features resemble the charge transfer bands observed in the spectra of $[M(bpy)_3]^{2+}$(M = Ru, Os) and related complexes.

In chapter **3**, the synthesis, characterization, electrochemical and ultraviolet spectral properties of multiisocyanide bridged by bis- and trismetallabenzenes and related complexes are investigated, and the plausible mechanism for the formation of chloro-substituted osmabenzenes is also presented. The chloro-substituted monoisocyanide coordinated osmabenzenes were synthesized by the reactions of the osmacycle $[Os(CH=C(PPh_3)CH(OH)-\eta^2-C\equiv CH)Cl_2(PPh_3)_2]$ with 2,6-dimethyl phenylisocyanide, p-tosylmethylisocyanide, 1H-benzotriazol-ylmethylisocyanide, 1,1,3,3-tetramethyl butylisonitrile, respectively. Following the reported procedure, four diisocyanides (1,4-phenylenediisocyanide, 4,4'-biphenyldiisocyanide, 4,4'-diisocyanodiphenylmethane, bis(4-isocyanophenyl)ether) were prepared in moderate yields. Additionally, the triisocyanide, 1,3,5-tris(4'-isocyanophenyl)benzene was prepared starting from the intermediate 1,3,5-tris(4'-aminophenyl)benzene under Ugi reaction conditions, which has not been reported before. The bis- and trismetallabenzenes $(\mu\text{-}(CN)_n\text{-}R)[M(CHC(PPh_3)CHC(PPh_3)CH)Cl_2(PPh_3)]_n[nPF_6]$ (M = Ru, Os: n = 2, R = 1,4-C_6H_4, 4,4'-$C_6H_4C_6H_4$, 4,4'-$C_6H_4CH_2C_6H_4$, 4,4'-$C_6H_4OC_6H_4$; n = 3, R = 1,3,5-(4'-C_6H_4)$_3$) have been synthesized by ligand substitution reactions of metallabenzenes with corresponding diisocyanide or triisocyanide ligands at room temperature in good yields, and the chloro-sunstituted bis and trisosmabenzenes $(\mu\text{-}(CN)_n\text{-}R)[M(CHC(PPh_3)CHC(Cl)CH)Cl(PPh_3)_2]_nCl_n$ (M = Os: n = 2, R = 1,4-C_6H_4, 4,4'-$C_6H_4C_6H_4$, 4,4'-$C_6H_4CH_2C_6H_4$, 4,4'-$C_6H_4OC_6H_4$; n = 3, R = 1,3,5-(4'-C_6H_4)$_3$) were obtained under reflux in dichloromethane via nucleophilic addition reactions in modest yields. With the similar method, two bisosmafuran complexes were also obtained in high yields. In addition, the electrochemical properties of bis- and trisosmabenzenes were investigated systematically, which revealed that the two metal centers in some complexes can interact with each other through diisocyanide bridges. UV-Vis studies showed a remarkable absorption in the region 310~360 nm for these complexes.